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THERMODYNAMICS, KINETICS AND EQUILIBRIUM SORPTION STUDIES OF THE ADSORPTION OF MERCURY IN HG^{2+}- RICE BRAN SYSTEM

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Abstract

Hg^{2+}ions from mining and urban runoffs can easily contaminate various water sources due to their high solubility in water. Due to its simplicity and viability, adsorption was utilized to treat Hg^{2+}ions -contaminated water using locally available rice bran as adsorbent. The adsorption behavior of the adsorbent was investigated using kinetics, thermodynamics and isotherm models. It was found that the adsorption of Hg^{2+}ions onto the adsorbent follows a pseudo-second order model and was best described by the Freundlich isotherm. The adsorption capacity was found to increase with increasing contact time, adsorbent dosage, temperature and with increasing initial Hg^{2+}ions concentration, with the highest adsorption capacity of 47.5 mg/L. The adsorption process was found to be spontaneous, endothermic and increases with temperature rise as the values obtained for thermodynamic parameters; ΔG, ΔH^o and ΔS^o are -1.36 x 10^{-3} $Jmol^{-1}$, 144.09 $Jmol^{-1}$ and 457.486 $Jmol^{-1}K^{-1}$, respectively. Results indicate that the freely abundant, locally available, low-cost adsorbent, rice bran could be economically viable for the removal of Hg^{2+} ions from mercury contaminated waste water.

Keywords: Thermodynamics, Mercury, Adsorption, Rice bran, Kinetics, Isotherm.

1.0 INTRODUCTION

Three different oxidation states abound for mercury: elemental (metallic, Hg^0), monovalent (mercurous, $Hg2^+2$) and divalent (mercuric, Hg^{2+}). Among the ionic forms, $Hg^{2+}$is most stable in the environment. The toxicity of mercury strongly depends on its redox state and is primarily associated with the divalentoxidation state (Itaru and Adams, 2004). The most consistent and pronounced effects of chronic exposure to mercury are neurological and psychiatric. Hence, the main result of mercury poisoning is damage of the central nervous system. This is primarily the consequence of reaction of mercury with sulfur atoms of brain proteins, enzymes, and other macromolecules, which results in perturbation of their function (Craig, 1986). Some other effects of mercury poisoning include kidney damage and dysfunction of the immune system(Itaru and Adams, 2004).

Numerous methods exist in the treatment of mercury laden waste water, nevertheless most are not preferred due to high costs, high energy consumption and difficulty of use (Wang *et al*., 2016; Dawlet *et al*., 2013; Karnib *et al*., 2014). Among the available methods, adsorption is proven to be one of the most economical and efficient (Karnib *et al*., 2014). It entails the adhesion of ions or molecules called the adsorbates onto a solid surface known as the adsorbent.

The choice of rice bran as adsorbent is anchored on its relative availability and biodegradability.

2.0 MATERIALS AND METHODS

Rice bran was collected and dried in direct sunlight for three days. The sundried bran was put in oven at 60^{o}C for twenty-four hours. The oven dried rice bran was thoroughly washed with distilled water to remove all dirt and was dried at 100^{o}C till constant weight. Then the dried bran was grinded and sieved with a 30-mesh sieve, to prepare homogenous particle size. The average particle size of adsorbents was measured and it was 496μm.

Stock solution of 50 mg/L of the adsorbate (Hg^{2+} ion) was prepared from the analytical grade of soluble salt of $HgCl_2$ which was accurately weighed and transferred into a known volumetric flask and serially diluted to obtain solutions between 10-30 mg/L. The experimental technique was carried out in a batch adsorption system.

1g of the adsorbent (rice bran) was added to each concentration between 10 to 30 mg/L, the resulting solutions were shaken continuously and left till the next day. It was filtered into a clean dried empty conical flask and labeled accordingly. The filtrates were taken for analysis of the metals (adsorbate concentrations) using already calibrated atomic absorption spectrophotometer (AAS).

In order to study the effect of adsorbent concentration on the rate of adsorption, 50 ml solution of the adsorbate was pipette from 50 mg/L into a conical flask followed by the dosage of different masses of the adsorbent between 1g to 8g and labeled accordingly. The resulting solutions were shaken continuously and left till the next day. Solutions were filtered into clean dried empty conical flasks and labeled accordingly. The filtrates collected in sample bottles were analyzed using AAS.

The effect of time was studied by following the procedure using 5g mass of adsorbent and 20mg/L solution of adsorbate. Minimum of five sets were set up and each experiment terminated at a specific time between 10-45 minutes. The temperature of solution was held constant at 20^{o}C with a thermostatic shaker. After different time intervals, the solutions were centrifuged. The clear filtrate obtained in each case was analyzed by using AAS. The effect of temperature on adsorption was also studied at six different temperatures; 30, 35, 40, 45, 50, 55, 60 and 65 °C.

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The amount of equilibrium adsorption, q_e*(mg /g)*, was calculated using the formula in equation 1,

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

The dye removal percentage was calculated using equation 2,

$$(\%) \text{ of dye removal} = \frac{(C_0 - C_e)}{C_0} \; x\, 100 \quad (2)$$

where $C_0$and Ce (mgL^{-1}) are the initial and equilibrium concentrations of the adsorbate in solution. w and v represent the mass of adsorbent and volume of solution, respectively.
The amount of sorption at time t, qt (mg/g), was calculated using equation 3,

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (3)$$

where C_t (mgL^{-1})is the liquid phase concentrations of adsorbate at any time,C_0(mgL^{-1}) is the initial concentration of the adsorbate in solution, *V* is the volume of the solution (L) and *W* is the mass of dry adsorbent in gram (Vijayakumar et al., 2012).

3.0 RESULTS AND DISCUSSION

3.1 Effect of Adsorbent Dose on Adsorption.

The effect of adsorbent dose on the adsorption of Hg^{2+} ion onto rice bran is depicted by Fig. 1. Hg^{2+} ions adsorption efficiency was found to increase with increase in adsorbent dose. This reveals that the adsorption sites remain unsaturated during the adsorption reaction whereas the number of sites available for adsorption site increases by increasing the adsorbent dose.

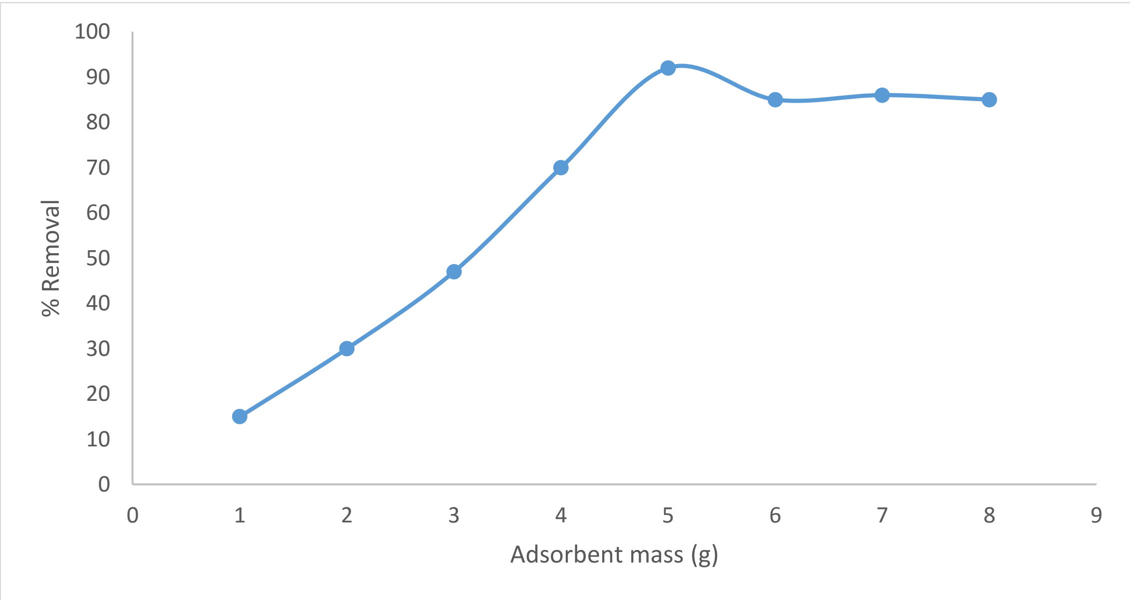

Fig. 1: Effect of adsorbent mass on adsorption

3.2. *Effect of Adsorbate Concentration*

The adsorption of Hg^{2+}ions onto rice bran has been investigated as a function of initial concentration. It was observed in figure 2 that maximum adsorption capacity increases with increasing initial Hg^{2+}ions concentration. Increasing the initial metal ion concentration increases the driving force to overcome the mass transfer resistance that hinders the movement of the metal ions from the bulk solution to the surface of the adsorbent. This allows for more metal ions to come into contact with the adsorbent particles (Soleimani and Siahpoosh, 2015). As a result, the adsorption capacity of the membrane increases as the initial metal ion concentration increases.

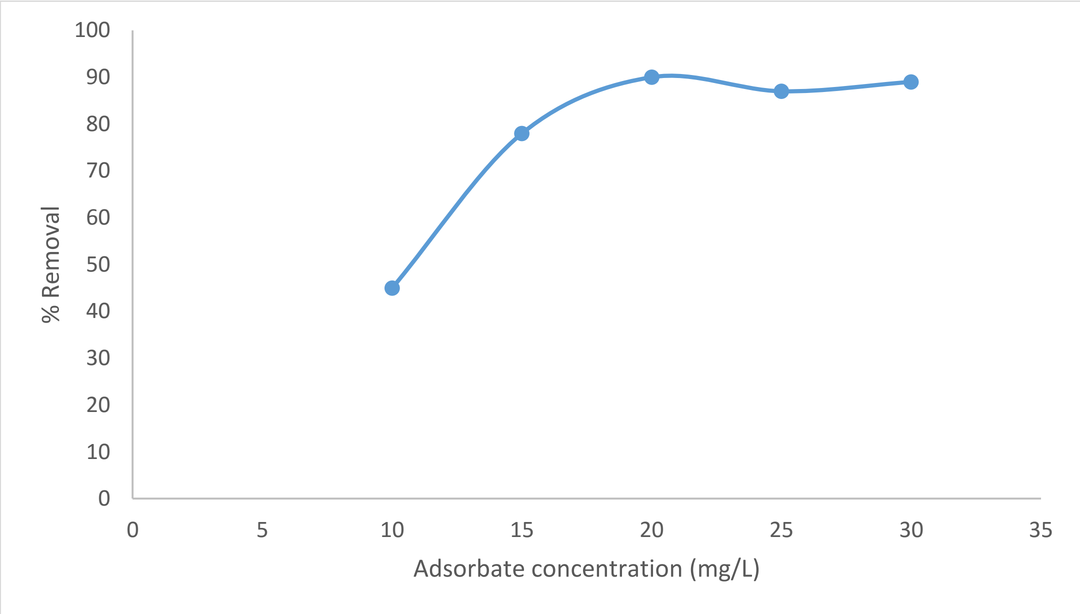

Figure 2: Effect of adsorbate concentration on adsorption

3.3 Effect of Contact Time

The adsorption of Hg^{2+} ions onto the adsorbent has been investigated as a function of time. Changes in the ion concentration were monitored at specific intervals from 10 to 40 minutes. Figure 3 shows the relationship between the adsorption capacity expressed as percentage removal and contact time at 20 mg/L of the adsorbate. It was observed that, the adsorption capacity increases with increasing contact time until no significant change in the adsorption capacity can be observed. A high initial removal was observed from the initial contact time up to 20 min. A slower removal followed until a plateau on the plot was observed, indicating equilibrium. This may be attributed to the high availability of adsorption sites at the start of adsorption. However, as adsorption progresses, the sites are gradually filled and ions have to intensely compete to be adsorbed (Benhammou *et al*., 2005).

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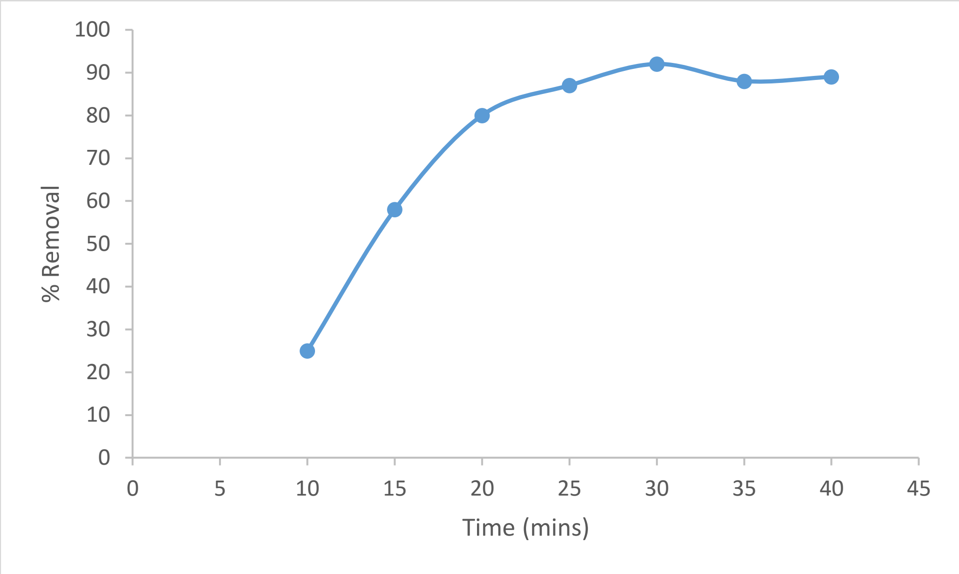

Fig. 3: Effect of Contact Time on Adsorption

3.4. *Effect of Temperature on Adsorption*

Effect of temperature on adsorption of Hg^{2+} ions onto the adsorbent was studied by conducting different sets of experiments at different temperatures. It was observed in Fig. 4 that adsorption of the metal ions increases with the increase in the temperature. The increase of adsorption with temperature could be due to changes in pore size of the adsorbent, causing intra-particle diffusion within the pore (Meena *et al*., 2008; Larous *et al*., 2005), or expansion within the active surface and site when the temperature increases [Meena *et al*., 2005, Larous *et al*., 2005]. It also could be explained that the movement of the metal to the adsorbent increases with an increase in temperature (Hsieh *et al*., 2006)

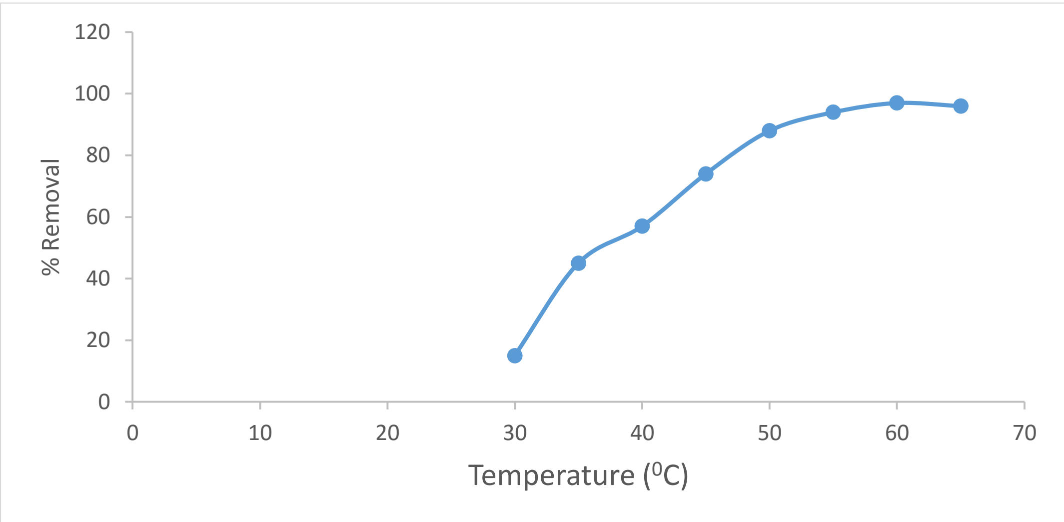

Fig. 4: Effect of Temperature on Adsorption

3.5Adsorption Isotherms

Though several adsorption isotherms abound for analyzing experimental sorption equilibrium parameters, the most common being the Langmuir and Freundlich models. The Langmuir isotherm model is based on the assumption that there is a finite number of active sites which are homogeneously distributed over the surface of the adsorbent. These active sites have the same affinity for adsorption of a mono molecular layer and there is no interaction between adsorbed molecules (Vijayakumar*et al*., 2012).

A well-known linear form of the Langmuir equation can be expressed as

$$\frac{1}{q_e} = \frac{1}{Q_{max}} + \frac{1}{b.Q_{max}} \cdot \frac{1}{C_e} \quad (4)$$

Q_{max} and b are Langmuir constants related to the maximum adsorption capacity (mg/g) and energy of adsorption (L/mg).

The Freundlich isotherm model applies to adsorption on heterogeneous surfaces with interaction between the adsorbed molecules, and is not restricted to the formation of a monolayer. This model assumes that as the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increases and, correspondingly, the sorption energy exponentially decreases on completion of the sorption centres of the adsorbent. The well-known expression for the Freundlich model is given as

$$\log q_e = \log k_f + \frac{1}{n}\log C_e \quad (5)$$

Kf is Freundlich constant related to the sorption capacity, and $1/n$ is an empirical parameter related to sorption intensity, which varies with heterogeneity of the material.

The Langmuir and Freundlich isotherms for the Hg^{2+} ion – rice bran system at 60^0Careshown in Figs. 5 and 6, respectively. The correlation coefficients were calculated by fitting the experimental equilibrium data for the system using both models. These results clearly show that the adsorption of Hg^{2+} ions on rice bran fits well with the Freundlich model. The fact that the Freundlich model is a good fit to the experimental adsorption data suggests physical adsorption as well as a heterogeneous distribution of active sites on the rice bran surface. The observed correlation coefficients for Langmuir and Freundlich isotherms were 0.8072 and 0.9685, respectively. The other Freundlich constant, n, is a measure of the deviation of the adsorption from linearity. If the value of n is equal to unity, the adsorption is linear. If the value of n is below unity, it implies that the adsorption process is unfavourable, and if the value of n is above unity, adsorption is favourable. In the present study, the value of n at equilibrium was above unity (n ≈ 8), suggesting favourable adsorption.

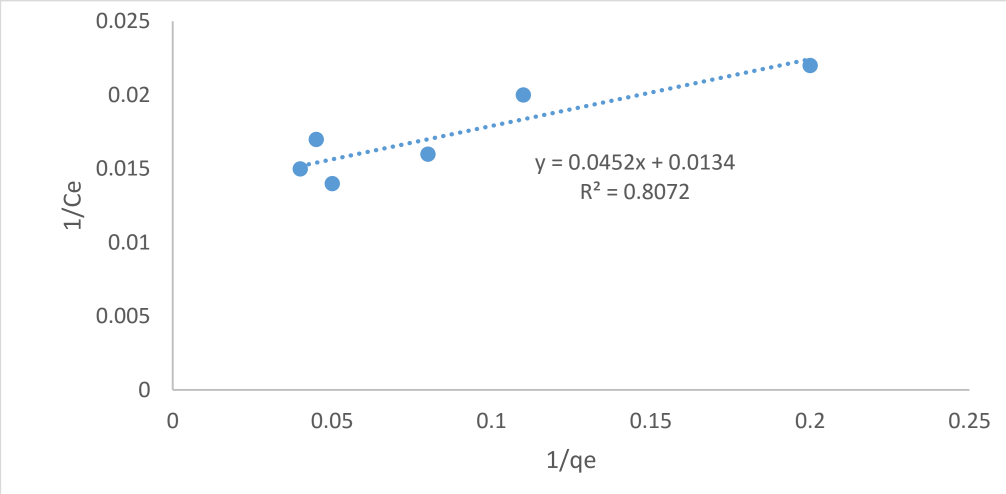

Figure 5: Langmuir Adsorption Isotherm plot for Hg^{2+} - rice bran system

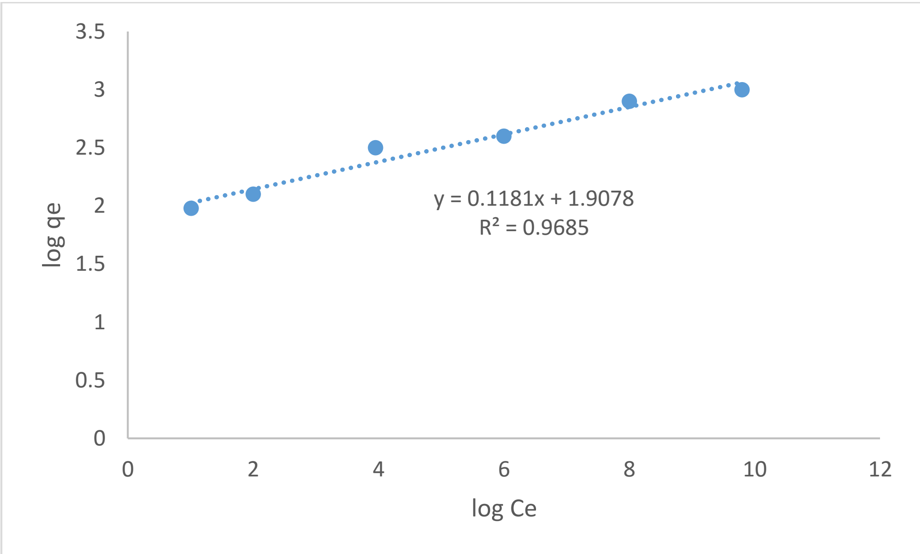

Figure 6: Freundlich Adsorption Isotherm plot for Hg^{2+} - rice bran system

3.6 Kinetic Studies

Numerous kinetic models have been proposed to elucidate the mechanism by which adsorbates are adsorbed on adsorbent. The mechanism of adsorption depends on the physical and / or chemical characteristics of the adsorbent, as well as on the mass – transport process. The rate constants of the adsorbate removal from the solution by the adsorbent were determined using first order and pseudo – second order equations. The lagergren first order rate equation was used to fit the experimental results. The integral form of the model is shown in equation 6.

$$\ln (q_e - q_t) = \ln q_e - k_1 t \qquad (6)$$

Where qe (mg/g) is the equilibrium sorption capacity and qt (mg/g) is the amount of Hg^{2+} ions adsorbed at time t (min), and k_1 is the equilibrium first-order constant. Values of k_1 forHg^{2+}

ions – rice bran system was obtained from the slope of the plot of *ln(qe-qt)* vs *t* (Figure (7)). The adsorption kinetic parameters from the figure indicates that $k_1 = 0.0504$ min^{-1}

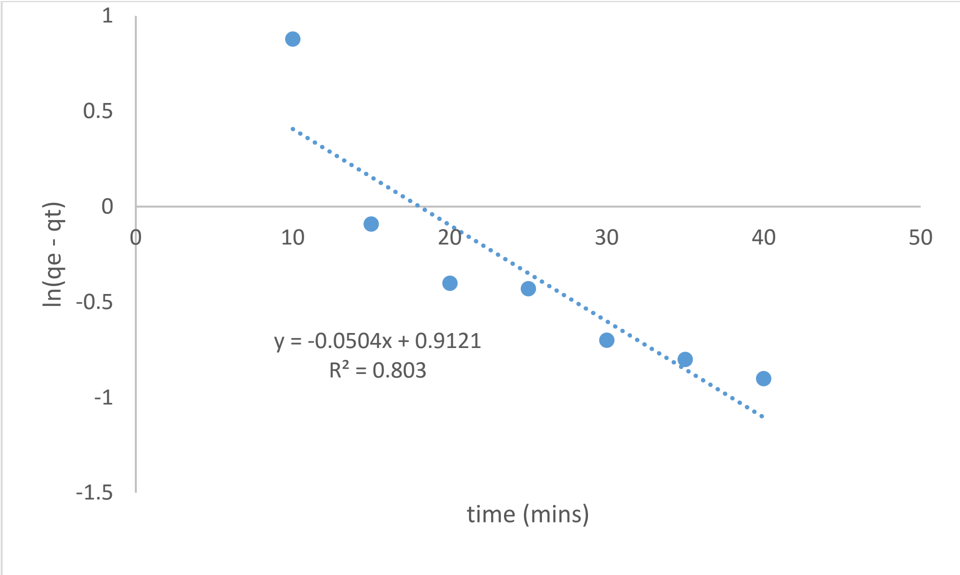

Figure 7: Lagergren first order kinetic plot for the adsorption of Hg^{2+} ions onto rice bran.

The adsorption data were also analyzed in terms of a pseudo-second order mechanism. The linearized integral form of this model is shown in equation 7.

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \left(\frac{1}{q_e}\right) t \qquad (7)$$

Where k_2(g.mg $^{-1}$.min^{-1}) is the rate constant of the pseudo – second order adsorption. If the initial adsorption rate is $k_2 {q_e}^2$, then equation (7) becomes equation (8);

$$\frac{t}{q_t} = \frac{1}{h} + \left(\frac{1}{q_e}\right) t \qquad (8)$$

Value of $k_2$for Hg^{2+} ions – rice bran system was obtained from the slope of the plot of t/qtvs. t (Figure (8)). The adsorption kinetic parameters from the Figure indicates that $k_2 = 0.33$ $gmg^{-1}min^{-1}$

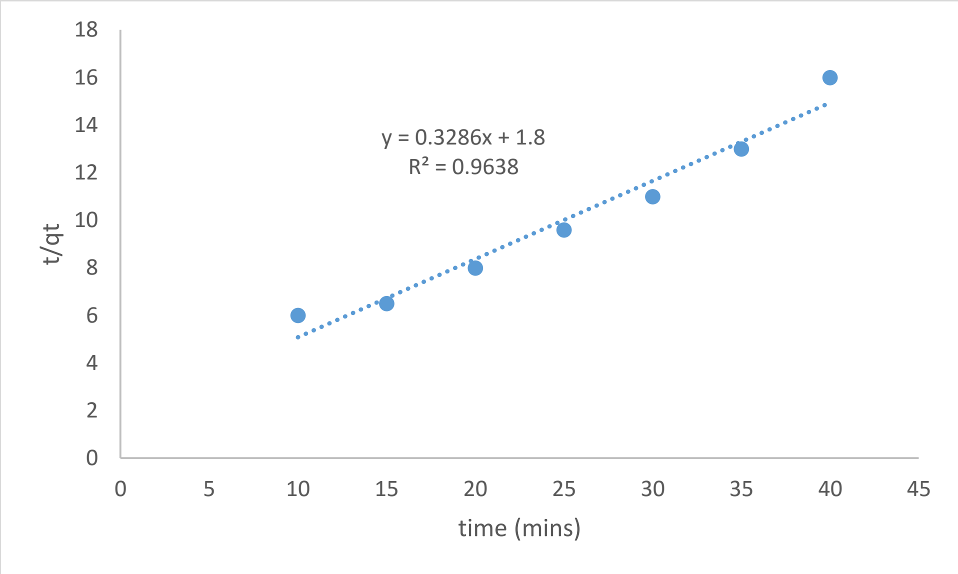

Figure 8: pseudo – second order kinetic plot for the adsorption of Hg^{2+} ions onto rice bran.

The linearity of these plots indicates the applicability of the two models. However, the correlation coefficients, R^2, show that the pseudo second order model fits the experimental data slightly better than the pseudo-first order model.

3.7 Thermodynamic Parameters

The effect of a change in temperature on the sorption system was studied to determine the thermodynamic parameters and to investigate the nature of the process. The sorption capacity increases with the temperature. Thermodynamic parameters for adsorption of Hg^{2+} ions onto rice bran such as heat of adsorption (enthalpy change, ΔH), entropy change, ΔS, free energy of specific adsorption and ΔG were calculated from the binding constant Kc obtained from the equations;

$\Delta G^o = \Delta H^o - T\Delta S^o$ (8)

But

$\Delta G^o = - RT \ln K_C$(9)

And $\ln K_C = \left(\frac{\Delta S}{R}\right) - \left(\frac{\Delta H}{R}\right)\frac{1}{T}$(10)

where

$K_C = C_{Ae}/C_{Se}$(11)

where K_C is the equilibrium constant, C_{Ae} is the amount of adsorbate on the adsorbent (mg/L), C_{Se} is the equilibrium concentration of adsorbate in the solution (mg/L), and R is the universal gas constant (8.314 J/mol /K). ΔH^o and ΔS^o were calculated from the slope and intercept of linear plot of $\ln K_C$ *versus* 1/T shown in figure 9. Extrapolation of the graph gives the values for ΔH^o and ΔS^o as 144.09 $Jmol^{-1}$ and 457.486 $Jmol^{-1}K^{-1}$, respectively. The free energy change accompanying the adsorption process was found to be -1.36×10^{-3} $Jmol^{-1}$. The Positive values of ΔH^o and ΔS^o are an indication that the adsorption process is endothermic and entropy of the Hg^{2+} ions – rice bran system increases with temperature. The negative value of ΔG indicates the spontaneous nature of adsorption. As the temperature increases, the ΔG values increase, indicating more driving force and hence resulting to greater adsorption capacity at higher temperatures.

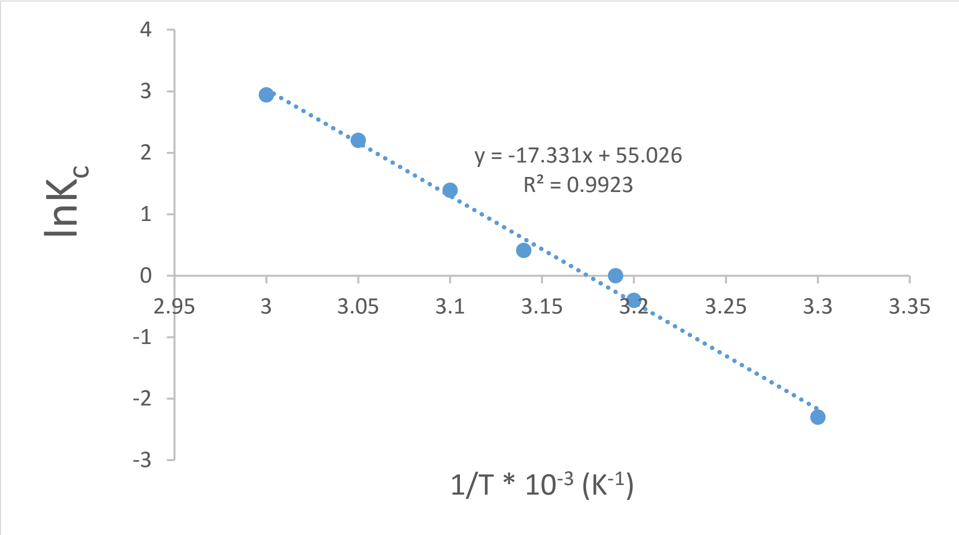

Figure 9: Plot of $\ln k_c$ against 1/T

4.0 Conclusion

Rice bran could be employed as environmentally friendly adsorbent in wastewater treatment for the removal of Hg^{2+} ions. The process of adsorption was found to increase linearly with adsorbent dose, adsorbate concentration, contact time and temperature. It was found that the adsorption of Hg^{2+}ions onto the adsorbent follows a pseudo-second order model and was best described by the Freundlich isotherm. The adsorption process was found to be spontaneous, endothermic and increases with temperature. The results of this research reveal that the freely abundant, locally available, low-cost adsorbent, rice bran could be economically viable for the removal of Hg^{2+} ions from mercury contaminated waste water.

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